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(71) Applicant(s)
Albright & Wilson UK Limited

(Incorporated in the United Kingdom)

P O Box 3, 210-222 Hagley Road West, Oldbury, WARLEY, West Midlands, B68 0NN, United Kingdom

(72) Inventor(s)
Keith Philip Davis
Alan Craig Smith
Michael John Williams

(74) Agent and/or Address for Service
Albright and Wilson UK Limited
PO Box 3, 210-222 Hagley Road West, Oldbury, WARLEY, West Midlands, B68 0NN, United Kingdom

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(54) Aqueous dispersion of a particulate solid

(57) A composition comprising a particulate solid which, in the absence of deflocculant, has a tendency to flocculate, and which is dispersed in a liquid aqueous medium, and at least one phosphono-carboxylic acid, or water soluble salt thereof, in an amount which is effective to inhibit flocculation of said particles, the phosphonocarboxylic acid having the general formula:

$H(CHR\ CHR)_n \cdot PO_3\ M_{2/v}$

wherein at least one R group in each unit is a $COOM_{1/v}$ group and the other R group(s) which may be the same or different is hydrogen, or a $COOM_{1/v}$, hydroxyl, phosphono, sulphono, C_{1-7} alkyl, C_{1-7} alkenyl group or a carboxylate, phosphono, sulphono, sulphato and/or a hydroxy substituted C_{1-7} alkyl or C_{1-7} alkenyl group, and each M is a cation such that the phosphonated carboxylate is water soluble v is the valency of M and n is from 1 to 6.

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DISPERSION OF SOLID PARTICLES IN WATER

The present invention relates to dispersions or slurries of solid particles in water and in particular to dispersions of mineral particles which normally tend to flocculate, and to a method of inhibiting the flocculation of such particles and thereby improving the pourability of the dispersions.

A variety of mineral particles such as, bentonite, e.g. for use in detergent formulations, talc for use as a filler in the paper industry or as an ingredient of cosmetic or toiletry formulations, clay for use in the ceramic industries and titanium dioxide for use in paints and coatings, are required in the form of pumpable slurries or dispersions in water, which tend to be viscous or immobile at the relatively high concentrations which are generally desirable, both technically and economically.

In order to obtain readily handleable products with sufficiently high solid concentrations, it has therefore been necessary to use additives which reduce the viscosity. These have included surface active dispersants which reduce interfacial tension within the system, strong alkalis to inhibit electrostatic interaction between the particles, inhibitors which prevent crystal growth, and deflocculants.

Among the latter are various organic polyelectrolytes, e.g. polycarboxylates such as polymaleates, and condensed phosphates such as sodium hexametaphosphate and sodium tripolyphosphate. In general the polymeric deflocculants are too expensive to be considered for many applications, while condensed phosphates are not sufficiently stable in certain media, e.g. paint formulations, to be useful in such systems.

It has been noted that certain phosphonocarboxylates e.g. 2-phosphono 1, 2, 4 - tricarboxybutane (hereinafter referred to as PTCB) tend to inhibit the flocculation of particles such as calcium carbonate. PTCB is, however a relatively expensive product.

There is a need for a product which is of comparable or superior deflocculating power to existing high performance polymeric dispersants, but cheaper, and which is more stable on prolonged storage than the condensed phosphates.

We have now discovered that flocculation of mineral, or other solid, particles in water is very effectively inhibited by certain phosphonation products of unsaturated carboxylic acids.

Our invention therefore provides a composition comprising a particulate solid which, in the absence of deflocculant, has a tendency to flocculate, and which is dispersed in a liquid aqueous medium, and a phosphonocarboxylic acid, or a water soluble salt thereof, in an amount which is effective to inhibit flocculation of said particles, wherein said phosphonocarboxylic acid has the formula:

$$H[CHRCHR]_n\text{-}PO_3M_2$$

wherein at least one R group in each unit is a $COOM_{1/v}$ group and the other R group is hydrogen or a $COOM_{1/v}$, hydroxyl, phosphono, sulphono, sulphato, C_{1-7} alkyl, C_{1-7} alkenyl group or a carboxylate, phosphono, sulphono, sulphato and/or hydroxy substituted C_{1-7} alkyl or C_{1-7} alkenyl group, and each M is a cation such that the phosphonated carboxylate is water soluble and n is from 1 to 6. Preferably n has value less than 5 e.g. 1 to 3.

The invention, according to a preferred embodiment uses a water soluble phosphono succinate or a phosphonated oligomer or mixture of phosphonated oligomers of maleic acid, of the formula $H(CHCO_2M.CHCO_2M)_nPO_3M_2$ where n is greater than 1 and M is a cationic species such that the oligomer is substantially water soluble, and especially mixtures of such oligomers with phosphonosuccinic acid or its substantially water soluble salts. The phosphonosuccinic acid preferably constitutes at least a major proportion by weight based on the total weight of the solvent-free mixture.

It is particularly preferred, according to the invention, to use phosphonated oligomers which comprise: at least 10%, preferably at least 50% by weight of a phosphonosuccinate based on the weight of the solvent-free composition; a phosphonated dimer of maleate; optionally a minor proportion by weight, relative to the weight of dimer, of higher phosphonated oligomers of maleate; and from 0.5 to 5% by weight of phosphate. A phosphonated oligomaleate reaction product of the above type having a mean degree of polymerisation between 1 and 1.5 will be referred to herein as POM.

The deflocculant may be prepared by reacting a carboxylate salt with a phosphite salt in aqueous solution in the presence of a free radical initiator. Such processes are described in GB-A-2252322 and EP-A-0569731. In general the deflocculant may be any of the products described in aforesaid patents, and especially the reaction product formed by reacting an alkali metal maleate with an alkali metal phosphite in the presence of a peroxide such as sodium persulphate or hydrogen peroxide.

The aforesaid preferred POM reaction product for use according to the invention may, for example, be prepared according to the teaching of Example 1 of EP-A-0569731.

The amount of deflocculant used may be from 0.01 to 10% by weight of the dispersed solid Higher concentrations could in some instances, be used but are unlikely to be cost effective.

Preferably the concentration based on the total weight of the solids is from 0.05 to 5%, more usually 0.1% to 3% most preferably 0.2% to 1%. With some deflocculants there is an optimum concentration above which the salt acts as a thickener. This optimum varies but typically lies between 0.3% and 0.8% by weight.

The Dispersed Solid

The dispersed or suspended solid may be any particulate solid which is sufficiently chemically inert to be dispersed or suspended in the aqueous medium. The particles are preferably inorganic, and substantially water insoluble e.g. a mineral such as an aluminosilicate or metal ore. Examples include talc, calcite, barite, mica, clays, shales, haematite, bauxite, magnetite, galena, copper or iron pyrites, coal, zeolite, titanium oxide and zinc oxide. The invention also covers the suspension of soluble or sparingly soluble solids in saturated aqueous solutions thereof.

The solid may, for example, be a detergent builder or fabric conditioner; a clay for use in the manufacture of ceramic articles, or an abrasive, pigment, dye, pesticide, cosmetic or pharmaceutical, or a weighting agent for oil well drilling muds. The dispersed particles may alternatively comprise a polymer, resin or latex, e.g. for use in paints and printing inks.

The particle size of the solid is preferably sufficiently small to enable the particles to be readily dispersed or suspended. For example we prefer that the particles size is less than 1mm e.g. less than 0 5mm preferably 0.5 to 100 micron especially 1 to 50 microns.

The proportion of solid may be from 1 to 90% by weight based on the total weight of the composition More usually the composition comprises from 10 to 80% preferably 20 to 70%, e.g. 30 to 65% by weight of suspended solid.

The Liquid Medium

The liquid medium may be water, optionally containing a dispersant such as a dilute surfactant or lignin sulphonate and/or suspending agent such as carboxymethyl cellulose or polyvinyl pyrrolidone.

The composition may, for example, be in the form of a mechanical dispersion, slurry, paste, clay or mud, or a sedimented dispersion capable of redispersion by shaking or stirring.

The pH of the liquid medium is usually neutral or alkaline e.g. greater than 7, preferably 8 to 14, especially 9 to 12.

The liquid medium may optionally contain water miscible or emulsifiable organic solvents, but they are not normally needed and unless specifically required, e.g. where the suspension is intended for use as a paint composition, they are preferably absent.

Pigment Suspensions

The invention is of particular value in providing mobile highly concentrated slurries of pigments, and especially of titanium oxide, for use as or in paints and other coating compositions.

According to a preferred embodiment there is provided a coating composition comprising: an aqueous based liquid vehicle; an organic binder comprising a drying oil or resin emulsified or interspersed with said liquid vehicle; particles of a pigment, which in the absence of a deflocculant, have a tendency to flocculate and which are suspended or dispersed in said liquid vehicle; and phosphono succinic acid, a phosphonated oligomer of an unsaturated carboxylic acid or a water soluble salt thereof in an amount sufficient to inhibit the flocculation of the pigment.

The preferred pigment is titanium oxide but any other pigment which has a tendency to flocculate may be used. For example, other useful pigments include, iron oxide, carbon black, phthalocyanine pigments or aluminium stearate. The pigment may comprise corrosion inhibiting pigments such as red lead, potassium zinc chromate, metallic zinc or aluminium powder or zinc oxide or zinc, calcium or aluminium phosphate, or citrates. The formulation may also contain polymers such as chlorinated rubber, polystyrene or silicone, asphalt, wetting agents, dispersants,

emulsifiers, biocides, marine antifoulants, antifoams, viscosifiers, fire retardants, fluorescers, aerosol propellants, extenders such as talc or clay and/or plasticisers.

The pigments are generally dispersed in paint, varnish, enamel, lacquer, or other coating formulation. The formulation may comprise a volatile liquid vehicle, such as water or a volatile organic solvent including petroleum spirit, turpentine, ketones, esters and/or aromatic hydrocarbon solvent, and/or a drying oil, such as linseed oil, soya oil, tung oil or dehydrated castor oil which may optionally be dissolved in said organic solvent or emulsified in said water. The formulation typically may also comprise a resin, or curable resin precursor, e.g. a polyester, urea formaldehyde, melamine, acrylic, alkyd, polyurethane, vinyl chloride, vinyl acetate, phenolic or epoxy resin dissolved or dispersed therein.

The deflocculant may be added to the pigment, or to an aqueous slurry thereof, prior to formulating the paint in order to provide the paint formulator with the pigment in a more readily and safely handleable and transportable form than either the powdery solid or a flocculated slurry thereof.

The invention may also provide bentonite slurries of improved mobility suitable for use in or as fabric conditioners e.g. in laundry applications, or for use in drilling muds, e.g. in drilling bore holes for oil wells. The invention also provides clay slips, e.g. kaolin, for ceramic use.

The invention is illustrated by the following examples:

Example 1

POM was compared with sodium hexametaphosphate (SHMP) and two commercial polycarboxylate deflocculants which are used to deflocculate titanium dioxide in the paint industry. 65% by weight titanium oxide was slurried in water with various concentrations of

deflocculant. Viscosity was measured at 25°C and 21 sec^{-1} shear rate using a "Carrimed" controlled stress rheometer with 4cm flat parallel plates and a 1mm gap. The results are set out in Table 1, all percentages are by weight and viscosities are expressed in Pa s.

Table 1

% Deflocc on Pigment	SHMP	POM	Polycarboxylate A	Polycarboxylate B
0	13.4	13.4	13.4	13.4
0.1	8.9	10.0	12.0	8.9
0.15	6.3	3.2	7.1	6.4
0.2	3.5	0.7	5.0	5.0
0.25	2.3	0.3	0.9	1.6
0.4	0.1	0.1	0.4	0.2
1.0	0.1	0.2	0.08	0.1

The POM according to the invention gave lower viscosities than the polymers in concentrations between 0.15 and 0.5%. Being comparatively inexpensive it provides a substantial advance in terms of cost effectiveness. The SHMP, although relatively cheap, is not sufficiently stable to withstand the long periods of storage to which paints are often subjected. In contrast POM has been found to possess the requisite stability.

Example 2

POM was compared with sodium amino trismethylene phosphonate (ATMP) and PTCB in a drilling mud comprising 15% by weight of bentonite in deionised water at increasing shear rate on a FANN viscometer. The results are recorded in Table 2. Percentages are expressed as weight of active acid based on the total weight of the mud.

The viscosities in Pa s are shown in Table 2.

Table 2

% Defloc	Shear Rate	Blank	POM	PTCB	ATMP
1.36	100 rpm	351.64	23.8	17.9	17.9
1.36	200 rpm	186.25	20.9	14.9	16.4
1.36	300 rpm	131.1	16.9	13.9	14.9
1.36	600 rpm	66.6	12.9	13.4	13.4
0.68	100 rpm	351.64	35.8	26.8	26.8
0.68	200 rpm	186.25	29.8	23.8	22.4
0.68	300 rpm	131.1	25.8	20.9	20.9
0.68	600 rpm	66.6	18.4	18.4	17.4
0.34	100 rpm	351.64	50.7	50.7	44.7
0.34	200 rpm	186.25	31.3	40.2	37.3
0.34	300 rpm	131.1	27.8	35.8	32.8
0.34	600 rpm	66.6	24.4	27.3	25.3
0.068	100 rpm	351.64	116.22	92.4	83.4
0.068	200 rpm	186.25	65.66	56.6	50.7
0.068	300 rpm	131.1	47.7	45.7	41.7
0.068	600 rpm	66.6	28.8	37.7	33.3

Example 3

The following formulation is a typical clay slip used for the manufacture of sanitaryware e.g. ceramic wash basins and toilets.

Component	%
Ball clay	18.3
China clay	20.8
Quartz	20.8
Nepheline syenlite	13.1
Water +	13.1
Deflocculant	27.22

The following samples were prepared:

1. Blank - no deflocculant
2. A mixture of Sodium Silicate/Sodium Carbonate at a ratio of 2:1 as a deflocculant.
3. POM as a deflocculant.

Viscosity measurements using a CARRIMED controlled stress rheometer gave the following viscosities (Pa.S) at a shear rate of 21 sec^{-1} at 25°C. A 4cm parallel plate was used.

<u>0.3% deflocculant solids to total solids</u>

Sample	Deflocculant	Viscosity (Pa.S)
1	None	Infinite, even at shear stress 500 Nm^{-2}
2	SiO_3/CO_3	0.0640
3	POM	0.0380

<u>0.2% deflocculant solids to total solids</u>

Sample	Deflocculant	Viscosity
1	None	Infinite, even at shear stress 500 Nm^{-2}
2	SiO_3/CO_3	0.0825
3	POM	0.0486

0.1% deflocculant solids to total solids

Sample	Deflocculant	Viscosity (Pa.S)
1	None	Infinite, even at shear stress 500 Nm^{-2}
2	SiO_3/CO_3	0.8900
3	POM	0.0612

0.05% deflocculant solids to total solids

Sample	Deflocculant	Viscosity (Pa.S)
1	None	Infinite, even at shear stress 500 Nm^{-2}
2	SiO_3/CO_3	9.0781
3	POM	0.6602

Example 4

The degree of flocculation of TiO_2 using the sodium salts of phosphonosuccinic acid and oligomers of unsaturated carboxylic acids containing 1.3 and 5.5 units was determined.

Sample	**Calculated molecular weight of sample**	**No of maleate units in sample**
X	286	1
Y	334	1.3
Z	1006.2	5.5

65% by weight titanium dioxide was slurried in water with various concentrations of deflocculant. The deflocculants were added at levels of 0.1, 0.15 and 0.2% deflocculant solids (sodium salts) to titanium dioxide. All the deflocculants were used in their fully neutralised (sodium) form. Visocisty measurements were conducted using a CARRIMED controlled stress

rheometer, the viscosities (Pa.s). being measured at a shear rate of 21 sec^{-1} at 25°C. A 3cm parallel plate was used.

Deflocculant	**Deflocculant level/ % w/w deflocculant to Ti02**			
	0	0.1	0.15	0.2
X	10.88	0.153	0.047	0.039
Y	10.88	0.336	0.043	0.039
Z	10.88	1.179	0.127	0.056

The results indicate that the deflocculant having shortest chain length, X, (i.e. lowest molecular weight) is the most active.

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CLAIMS

1. A composition comprising a particulate solid which, in the absence of deflocculant, has a tendency to flocculate, and which is dispersed in a liquid aqueous medium, and at least one phosphonocarboxylic acid, or water soluble salt thereof, in an amount which is effective to inhibit flocculation of said particles, characterised in that said phosphonocarboxylic acid has the general formula

$$H[CHR\ CHR]_n - PO_3 M_{2/v}$$

wherein at least one R group in each unit is a $COOM_{1/v}$ group and the other R group(s) which may be the same or different is hydrogen, or a $COOM_{1/v}$, hydroxyl, phosphono, sulphono, C_{1-7} alkyl, C_{1-7} alkenyl group or a carboxylate, phosphono, sulphono, sulphato and/or a hydroxy substituted C_{1-7} alkyl or C_{1-7} alkenyl group, and each M is a cation such that the phosphonated carboxylic acid is water soluble, v is the valency of M and n is from 1 to 6.

2. A composition according to Claim 1 where n has an average value of from 1 to 3.

3. A composition according to Claim 2 wherein said phosphonocarboxylic acid is phosphonosuccinic acid.

4. A composition according to either of Claims 1 and 2 wherein said phosphonocarboxylic acid is a phosphonated oligomer of an unsaturated carboxylic acid.

5. A composition according to Claim 4 wherein said phosphonated oligomer is a phosphonated oligomer of maleic acid of the formula $H(CHCO_2M\ CHCO_2M)_nPO_3M_2$ where n is greater than 1 and M is a cationic species such that the compound is substantially water soluble.

6. A composition according to any foregoing claim wherein said composition comprises from 0.01 to 10% by weight based on the weight of the dispersed solid of said phosphono-carboxylic acid.

7. A composition according to any of Claims 1 to 4 wherein said composition comprises from 1 to 90% of said solid by weight based on the total weight of the composition.

8. A composition according to any of the foregoing claims wherein said solid is selected from the group comprising inorganic minerals, detergent builder, fabric conditioner, clay, abrasive, pigment, dye, pesticide, pharmaceutical, cosmetic, weighting agent, polymer, resin, latex.

9. A composition according to any of the foregoing claims, wherein said liquid medium comprises a dispersant selected from the group comprising a surfactant, a lignin sulphonate and a suspending agent or a mixture thereof.

10. A composition according to any of the foregoing claims wherein the pH of the liquid medium is neutral or alkaline.

11. A composition according to any of the foregoing claims wherein said salt is the sodium or potassium salt.

12. A coating composition according to any foregoing claim comprising: an aqueous based liquid vehicle, an organic binder comprising a drying oil or resin emulsified or interspersed with said liquid vehicle; particles of a pigment, which, in the absence of a deflocculant, have a tendency to flocculate and which are suspended or dispersed in said liquid vehicle; and at least one phosphonocarboxylic acid or a water soluble salt thereof in an amount sufficient to inhibit the flocculation of the pigment.

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The Patent Office

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Other: ON-LINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB1598529 BAYER	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.